

# Kinetics of reactions of ground state nitrogen atoms ( $^4S_{3/2}$ ) with NO and NO<sub>2</sub>

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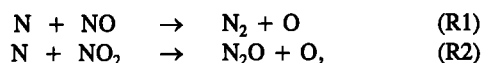
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**Abstract.** The discharge flow technique has been used with resonance fluorescence detection of N atoms to study the fast radical-radical reaction of ground state nitrogen atoms ( $^4S_{3/2}$ ) with NO and NO<sub>2</sub>. The rate constants obtained are (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)  $k_1 = (2.2 \pm 0.2) \times 10^{-11} \exp[(160 \pm 50)/T]$  in the temperature range 213 K  $\leq T \leq$  369 K for N + NO  $\rightarrow$  N<sub>2</sub> + O and  $k_2 = (5.8 \pm 0.5) \times 10^{-12} \exp[(220 \pm 50)/T]$  in the temperature range 223 K  $\leq T \leq$  366 K for N + NO<sub>2</sub>  $\rightarrow$  N<sub>2</sub>O + O. The reported error limits are at the 95% confidence level. The reaction kinetics are consistent with other radical-radical reactions, essentially no enthalpic barrier is observed. Substitution of the measured rate of R<sub>1</sub> for the value recommended in the latest Jet Propulsion Laboratory compendium [DeMore *et al.*, 1992] results in a small change in the concentration of ozone predicted in a two-dimensional photochemical model. Modeled ozone concentrations are higher (approximately 1%) in the high-latitude upper stratosphere as a result of a 3–10% reduction in the calculated concentrations of NO<sub>x</sub>.

## Introduction

The reactions of ground state nitrogen atoms ( $^4S_{3/2}$ ) with nitric oxide and nitrogen dioxide,



are of importance in atmospheric chemistry [Brasseur and Solomon, 1986] as well as in attempts to determine the relationship between electronic structure and reactivity [Howard and Smith, 1983]. Understanding these processes, however, has been hindered by the large uncertainty in the measured rate constants; despite numerous studies of these reactions the kinetics are poorly defined.

Reaction (R1) is the dominant removal mechanism for odd nitrogen in the upper stratosphere and mesosphere. It is this reaction that prevents the upper atmosphere from being a significant source of NO<sub>x</sub> for the stratosphere. Because the atmospheric source of nitrogen atoms is the photolysis of NO, (R1) has been dubbed “cannibalistic” as it results in the loss of two odd nitrogen molecules [Brasseur and Solomon, 1986]. Reaction (R2) plays a far less significant role in stratospheric chemistry because of the small concentration of NO<sub>2</sub> in the upper stratosphere.

The reactions of radicals with NO and NO<sub>2</sub> constitute the most studied series of radical-radical reactions [Howard and Smith, 1983]. By examining a series of homologous reactions, insight can often be gained about the reaction mechanism and the potential energy surface. This analysis is greatly enhanced

by knowledge of the temperature dependence of the reaction rates. This work reports the temperature dependence of the title reactions over the range of 213–369 K, including the first such study of (R2).

Although these two reactions have been studied extensively (see Tables 2 and 4), there is still large uncertainty in the rates. There is general agreement on the room temperature rate constant for (R1), but the two direct studies of the temperature dependence below 300 K disagree [Clyne and McDermid, 1975; Lee *et al.*, 1978]. There is little consensus about the value of the room temperature rate constant for (R2). A recent evaluation gives an uncertainty of  $\pm 300\%$  [DeMore *et al.*, 1992]. The results of the latest direct studies of this reaction differ by more than an order of magnitude [Clyne and Ono, 1982; Husain and Slater, 1980].

Previous attempts to measure these reaction rates have been hindered by poor detection efficiency and complications due to impurities in discharge and photolytic N-atom sources. In these studies we have employed a gas filter scheme that allows for selective resonance fluorescence detection with very high sensitivity. The low wall reactivity of N atoms was exploited to produce a discharge source free of radical impurities. This combination of a clean N-atom source and low detection limits allowed us to use initial radical concentrations more than 1 order of magnitude lower than previous studies without compromising on precision. The 2 $\sigma$  confidence limits (based on precision alone) for all the experiments was less than 3%.

## Experiment

The discharge flow system used in these studies has been described in detail elsewhere [Brune *et al.*, 1983]. Briefly, the reactor is composed of two sections of Pyrex tubing separated by a laser magnetic resonance (LMR) axis not used in this work.

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The kinetics were carried out in a 70-cm-long, 25-mm-ID flow tube that is jacketed to allow for chilled or heated fluid to be circulated for thermal control. After the LMR axis the radicals pass into the resonance fluorescence (RF) block, which houses three detection axes. For these experiments the gaps in the LMR and first RF axis were sealed with Pyrex tubes to minimize the radical losses. All reactor surfaces are coated with Teflon.

In the determination of the rate constants, NO and  $NO_2$  were added in excess ( $[NO]$  or  $[NO_2] \gg [N]_0$ ) at the back of the reaction zone. The nitrogen atoms were produced in a microwave discharge of trace  $N_2$  in He and added to the flow tube through a movable Pyrex 7-mm-OD injector. The reaction time was varied by changing the location of the addition of the N atoms. Because of the very low wall reactivity of N atoms the interior wall of the probe was not coated with Teflon. This produced a pure source of ground state N atoms; in the probe, there was nearly complete removal of the H and O impurities produced in the discharge. The long residence time in the probe (approximately 300 ms) also ensured that excited states of N were quenched by wall collisions before being added into the bulk flow.

### Resonance Fluorescence Lamps

Nitrogen atom densities were measured by resonance fluorescence. The RF lamp consisted of a quartz body with a  $MgF_2$  window. The resonance radiation was produced in a microwave discharge of trace quantities of  $N_2$  in about 2 torr of He. A pump was used to maintain a slow gas flow through the lamp. The 1200 Å  $^4P - ^4S$  (3s-2p) resonant emission from the lamp was isolated from lines due to O and other excited states of N by flowing  $CO_2$  at a pressure of 1000 torr through a 3-mm gas filter cell located in front of the lamp. Hydrogen impurities in the lamp produced Ly- $\alpha$  radiation at 1216 Å that is not absorbed by the  $CO_2$ . By replacing the  $CO_2$  filter gas with  $O_2$ , which strongly absorbs all but Ly- $\alpha$ , the ratio of the 1216- to 1200-Å light could be measured. In no case did this ratio exceed one third. With  $O_2$  in the gas filter cell the lamp could be used to diagnose atomic hydrogen production by the N source. The H atom concentrations in the flow tube were less than  $1 \times 10^8$  atoms  $cm^{-3}$ . Resonance fluorescence was detected with a KBr photomultiplier tube (EMR 541J) operated in photon counting mode.

Oxygen atoms were detected with a sealed combination O and H lamp, which has been described elsewhere [Brune *et al.*, 1983]. To isolate the oxygen triplet at 1304 Å from the hydrogen Ly- $\alpha$ , a  $CaF_2$  filter was inserted in front of the lamp. A flow of dry  $N_2$  was maintained in the gas filter cell to prevent damage to the  $MgF_2$  windows. The lamp was calibrated by titrating a known density of NO with excess N atoms. Sensitivity of the lamp was  $8 \times 10^{-9}$  (counts  $s^{-1}$  / (atom  $cm^{-3}$ )) with background signals typically  $< 100$  counts  $s^{-1}$  giving a detection limit of  $3 \times 10^9$  atoms  $cm^{-3}$ . The N lamp was then calibrated by measuring the N-atom sensitivity relative to the O lamp using the NO titration. The responsivity of this lamp for N was typically  $3 \times 10^{-7}$  (counts  $s^{-1}$  / (atom  $cm^{-3}$ )) with a scattered-light count of  $< 100$  counts  $s^{-1}$  resulting in a detection limit of less than  $1 \times 10^8$  atoms  $cm^{-3}$ .

### Materials

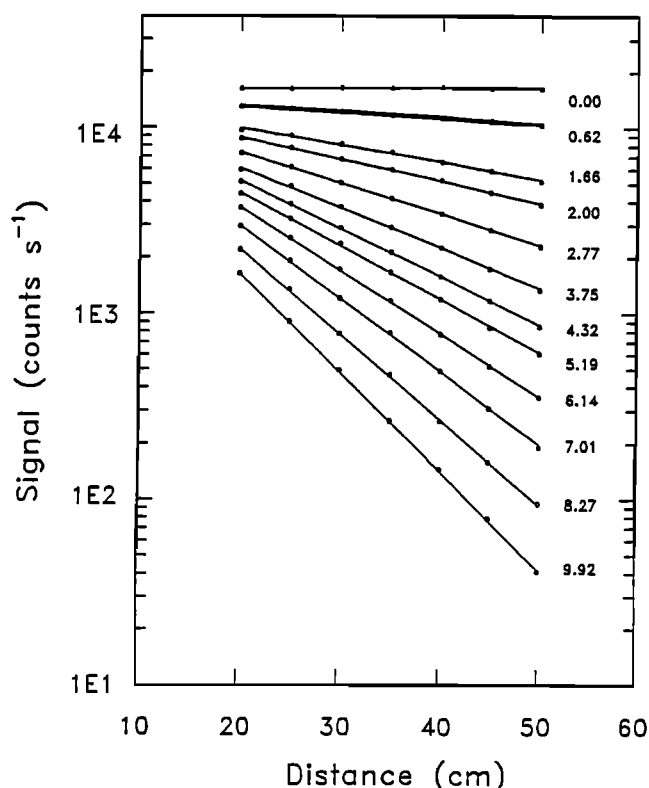
The following gases were used with their stated purities: He (HP, 99.99%) for bulk flow; He (UHP, 99.999%) and  $N_2$  (UHP, 99.999%) for the discharge source and excess reagent

mixtures; He (99.9999%) and  $N_2$  (UHP, 99.999%) for the flowing lamp. All gases were supplied by Matheson except the HP and UHP He and the UHP  $N_2$ , which were supplied by Northeast Airgas. NO (CP, 99.0%) and  $NO_2$  (99.5%) were provided by Matheson and purified before used as follows: NO was passed through a sodium-hydroxide coated silica (Ascarite) trap and then over potassium hydroxide, which was cooled to  $-50^\circ C$ ;  $NO_2$  was passed over a trap at  $-40^\circ C$  and then collected at  $-196^\circ C$ . The condensate was then warmed to  $-60^\circ C$  to allow any NO to be pumped off. The  $NO_2$  was then sublimed into the reservoir. NO and  $NO_2$  concentrations in the flow tube were determined by monitoring the rate of pressure drop in reservoirs of known volumes. The  $NO_2$  concentration was corrected for  $N_2O_4$  formation using JANAF thermochemical data [Chase *et al.*, 1985]. Because of the low pressures of  $NO_2$  used to make up the reservoirs ( $< 10$  torr), this correction was small ( $< 10\%$ ).

### Data Analysis

The pseudo first order decay rates ( $k_{obs}^I(x)$ ) were obtained from a weighted least squares fit of the logarithm of the detected signal minus the background chamber scatter versus injector distance. Typical N atom decays are shown in Figure 1. The initial N concentrations for this set of decays was  $5 \times 10^{10}$  atoms  $cm^{-3}$ , which was typical of all the experiments. Using the plug flow approximation, the reaction distance is directly convertible to reaction time and so,

$$k_{obs}^I(t) = \bar{v} \times k_{obs}^I(x).$$



**Figure 1.** Pseudo-first-order N atom decays in excess  $NO_2$ .  $T = 298$  K;  $P = 1.7$  torr. Distances are directly converted to reaction time (using the plug-flow approximation) from the bulk velocity,  $\bar{v} = 9.03 \times 10^2$  cm  $s^{-1}$ . Given at the right are  $NO_2$  concentrations in units of  $10^{12}$  molecules  $cm^{-3}$ . The quality of the data shown is typical of all the experiments reported.

**Table 1.** N + NO → N<sub>2</sub> + O

Condition	Result
Observed rate constant $k_1$	$(2.2 \pm 0.2) \times 10^{-11} \exp[(160 \pm 50)/T]$ for 213 K ≤ $T$ ≤ 369 K
Number of experiments	11 at 369 K $(3.30 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 13 at 334 K $(3.52 \pm 0.05) \times 10^{-11}$ 40 at 298 K $(3.65 \pm 0.08) \times 10^{-11}$ 12 at 273 K $(3.68 \pm 0.14) \times 10^{-11}$ 12 at 253 K $(3.94 \pm 0.15) \times 10^{-11}$ 10 at 237 K $(4.19 \pm 0.05) \times 10^{-11}$ 12 at 228 K $(4.38 \pm 0.06) \times 10^{-11}$ 12 at 213 K $(4.56 \pm 0.04) \times 10^{-11}$
Pressure range	1.0 – 4.0 torr
Flow velocity range	6.8 – 11.1 m s <sup>-1</sup>
Carrier gas	He
Diffusion coefficient	N – He, $0.158 T^{3/2}/P$ (< 8% correction)
Species detected	N (RF) O (RF) H (RF)
Excess reactant	[NO] = $(0.5 - 5.0) \times 10^{12} \text{ molecules cm}^{-3}$
Initial N concentration	[N] <sub>0</sub> = $(0.3 - 1.0) \times 10^{11} \text{ atoms cm}^{-3}$
Stoichiometric ratio	4 – 150
Observed first-order wall removal rates	< 1 s <sup>-1</sup>

The decay rates were then corrected for axial diffusion [Howard, 1979]:

$$k' = k_{\text{obsd}}^I(t)[1 + k_{\text{obsd}}^I(t)D / \bar{v}^2]$$

where  $\bar{v}$  is the mean bulk flow velocity and  $D$  is the radical diffusion coefficient ( $D = 4.1 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$  for N atoms in helium at 298 K and 2.0 torr [Clyne and Ono, 1982]). The diffusion correction was small and did not change the calculated bimolecular rate constant by more than a few percent. The correction did, however, significantly increase the precision. After subtraction of the chamber-scatter component of the signal, pure-exponential decays were observed for over 5 e-foldings of the N atom concentrations.

## Results and Discussion

### N + NO → N<sub>2</sub> + O

Table 1 summarizes the experimental conditions and results for this reaction. The plot of  $k'$  versus NO for all the room temperature data is shown in Figure 2. A weighted least squares fit of the data yields a value of

$$k_1^{298} = (3.63 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

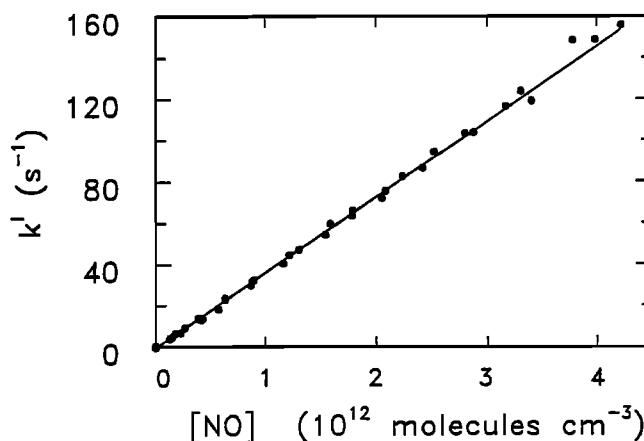
for the bimolecular rate constant for (R1). The precision of the measured pseudo-first-order rate constant,  $k'$ , gives the 2σ experimental uncertainty quoted. With the addition of other uncertainties and including an estimate of systematic errors (due to pressure and flow measurement errors) we report

$$k_1^{298} = (3.6 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}.$$

The temperature dependence of the bimolecular rate constant ( $k_1^H$ ) was determined between 213 and 369 K and was found to be slightly negative, i.e.,  $k_1$  increases with decreasing temperature. The Arrhenius plot is shown in Figure 5. From a weighted least squares fit of all the data, including an estimate of systematic errors, we find

$$k_1^H = (2.2 \pm 0.2) \times 10^{-11} \exp[(160 \pm 50)/T] \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}.$$

Table 2 gives previous measurements of this rate constant near and below room temperature. The measured room temperature rate is consistent with most previous measurements. In general, the rate constants obtained with mass spectroscopy determination are lower, and the flash photolysis results are higher than studies employing discharge flow/resonance fluorescence.



**Figure 2.** Plot of  $k'$  versus NO concentration at room temperature. Data are for experiments done at pressures between 1 and 4 torr.

**Table 2.** Literature Comparison for N + NO → N<sub>2</sub> + O (200 K < T < 400 K)

Reference	$k(298)^a$	$k(T)^a$	Method <sup>b</sup>
This work	$3.6 \pm 0.4$	$(2.2 \pm 0.2) \exp[(160 \pm 50)/T]$	DF-RF
<i>Clyne and Thrush</i> [1961]	–	$5.0 \exp[(-100 \pm 350)/T]$	relative
<i>Herron</i> [1961]	$1.7 \pm 0.8$	–	DF-MS
<i>Lin et al.</i> [1970]	$3 \pm 1$	–	KS
<i>Clyne and McDermid</i> [1975]	$2.2 \pm 0.2$	$(8.2 \pm 1.4) \exp[(-410 \pm 120)/T]$	DF-MS
<i>Lee et al.</i> [1978]	$4.0 \pm 0.5$	$(3.2 \pm 0.2) \exp[(65 \pm 20)/T]$	FP-RF
<i>Lee et al.</i> [1978] <sup>c</sup>	$3.0 \pm 0.2$	$(1.7 \pm 0.4) \exp[(150 \pm 50)/T]$	DF-RF
<i>Sugawara et al.</i> [1980]	$1.9 \pm 0.2$	–	PR-RA
<i>Cheah and Clyne</i> [1980]	$3.4 \pm 0.6$	–	DF-RF
<i>Husain and Slater</i> [1980]	$4.5 \pm 0.2$	–	FP-RF
<i>Clyne and Ono</i> [1982]	$2.8 \pm 0.1$	–	DF-RF
<i>Bunning and Clyne</i> [1984]	$2.0 \pm 0.3$	–	DF-MS
<i>DeMore et al.</i> [1992]	$3.4 \pm 1.0$	$(3.4 \pm 1.0) \exp[(0 \pm 100)/T]$	review

<sup>a</sup>  $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>b</sup> FP, flash photolysis; DF, discharge flow; KS, kinetic spectroscopy; PR, pulsed radiolysis; RF, resonance fluorescence; RA, resonance absorption; MS, mass spectroscopy.<sup>c</sup> Data corrected for axial diffusion and fit by weighted least squares analysis.

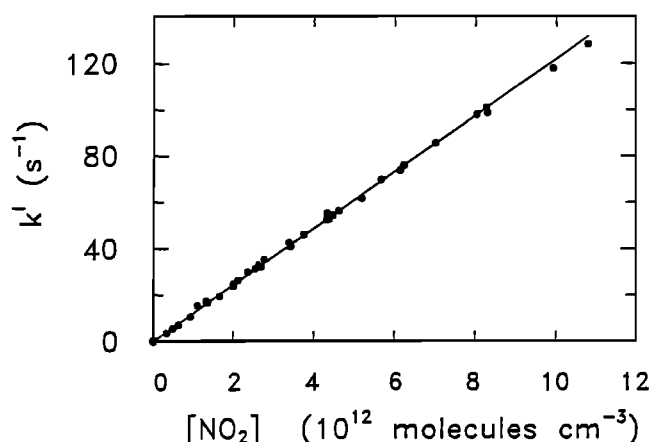
*Lee et al.* [1978] measured this reaction by both discharge flow and flash photolysis. The rate determined in their flash photolysis study was 50% higher than the rate from discharge flow. In their discharge flow experiment the calculated rate constant was seen to increase slightly with pressure, and this pressure dependence was suggested to explain the difference in the measured rate constants. However, no axial diffusion correction was used in their data analysis of the discharge flow experiments. Correcting their data increases the rate constant and removes the observed pressure dependence. In this work, no statistically significant difference in the calculated bimolecular rate constant was seen for the different pressures once the diffusion correction was applied. The data shown in Figure 2 include experiments done at 1, 2, and 4 torr.

The rate constants measured by flash photolysis are systematically higher than studies employing discharge flow. Both *Lee et al.* [1978] and *Husain and Slater* [1980] used N<sub>2</sub>O as the source for N atoms. This source produces only excited states of N. In addition, the primary photoproduct is excited state oxygen atoms [*Okabe*, 1978]. It is likely that the presence of these excited state species complicates the kinetics, enhancing the determined rate constants.

The temperature dependence measured in this work is in agreement with *Lee et al.* [1978] who observed a slight increase of the rate with decreasing temperature in both discharge flow and flash photolysis experiments. A weighted least squares fit of the diffusion-corrected data of *Lee et al.* yields an Arrhenius expression of  $(1.7 \pm 0.4) \times 10^{-11} \exp[(150 \pm 50)/T]$  for the dis-

**Table 3.** N + NO<sub>2</sub> → N<sub>2</sub>O + O

Condition	Result
Reported rate constant $k_1$	$(5.8 \pm 0.5) \times 10^{-12} \exp[(220 \pm 50)/T]$ for 223 K ≤ T ≤ 366 K
Number of experiments	14 at 366 K $(1.04 \pm 0.01) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 13 at 328 K $(1.13 \pm 0.01) \times 10^{-11}$ 50 at 298 K $(1.20 \pm 0.02) \times 10^{-11}$ 14 at 270 K $(1.31 \pm 0.02) \times 10^{-11}$ 14 at 248 K $(1.42 \pm 0.02) \times 10^{-11}$ 14 at 223 K $(1.52 \pm 0.02) \times 10^{-11}$
Pressure range	1.0 – 3.0 torr
Flow velocity range	6.9 – 11.0 m s <sup>-1</sup>
Carrier gas	He
Diffusion coefficient	N – He, $0.158 T^{3/2}/P$ (< 8% correction)
Species detected	N (RF) O (RF) H (RF)
Excess reactant	[NO <sub>2</sub> ] = $(0.05 - 1.20) \times 10^{13} \text{ molecules cm}^{-3}$ [N] = $(2.5 - 4.0) \times 10^{12} \text{ atoms cm}^{-3}$
Initial N concentration	[N] <sub>0</sub> = $(0.2 - 1.0) \times 10^{11} \text{ atoms cm}^{-3}$
Stoichiometric ratio	4 – 400; 0.1 – 0.05
Observed first-order wall removal rates	< 1 s <sup>-1</sup>



**Figure 3.** Plot of  $k'$  versus NO<sub>2</sub> concentration at room temperature. Data are for experiments done at pressures between 1 and 4 torr.

charge flow experiment and  $(3.2 \pm 0.2) \times 10^{-11} \exp[(65 \pm 30)/T]$  for the flash photolysis experiment. The temperature dependence does not agree with the work of *Clyne and McDermid* [1975]. They reported a positive temperature dependence with an activation energy of 0.8 Kcal / mol. In that experiment, N atoms were detected by mass spectroscopy with poor sensitivity.

Three high temperature studies of this reaction have recently been published [*Koshi et al.*, 1990; *Davidson and Hanson*, 1990; *Michael and Lim*, 1992]. These were shock tube experiments employing resonance absorption detection of N. In excellent agreement with the results reported here, Koshi et al. obtained a rate constant of  $(2.2 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 1600 to 2300 K. Michael and Lim report a temperature independent rate of  $(3.7 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  over the temperature range 1540 to 2500 K. Davidson and Hanson report  $k_1 = 7.13 \times 10^{-11} \exp(-787/T)$  for  $1400 \text{ K} \leq T \leq 3500 \text{ K}$ . Because of the very different reaction energies the disagreement with the Arrhenius expression determined in this work may not be significant.

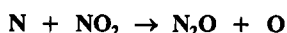


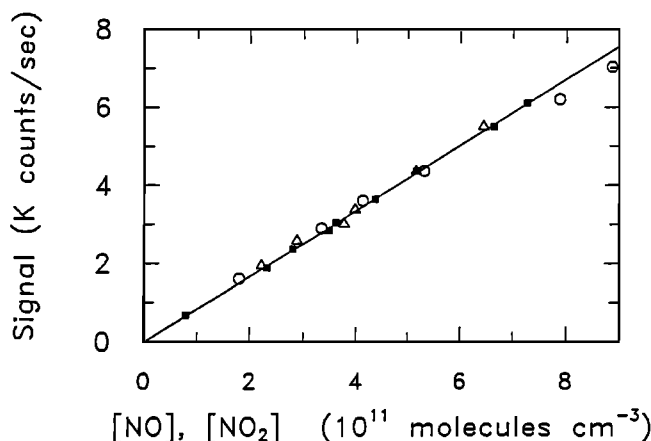
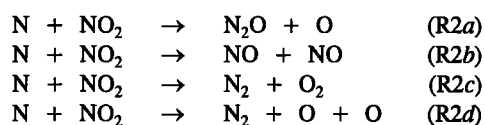
Table 3 gives a summary of the results for (R2). A plot of  $k'$  versus NO<sub>2</sub> for all the data taken at room temperature is shown in Figure 3. Included are experiments with initial N concentrations as low as  $2 \times 10^{10} \text{ atoms cm}^{-3}$ . No pressure dependence was observed between 1 and 3 torr. A weighted least squares fit of the data yields a value for the bimolecular rate constant of

$$k_2^{298} = (1.22 \pm 0.02) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

where the error quoted is  $2\sigma$  and represents the precision in the measurement of  $k'$ . With the addition of uncertainties due to flow and pressure measurements,

$$k_2^{298} = (1.2 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}.$$

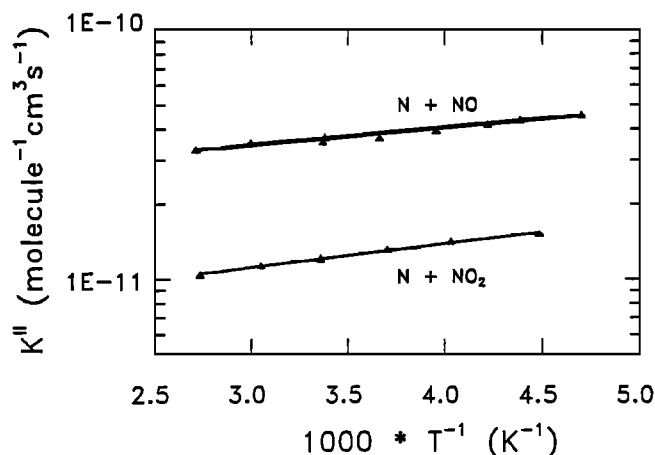
Reaction (R2) has four thermodynamically accessible channels:



**Figure 4.** Yield of oxygen atoms from the reaction of N with NO<sub>2</sub> (triangles and circles) versus the reaction with NO (solid squares) in excess N. Reaction (R1) is known to have unit quantum yield. Two different concentrations of N were used: squares, circles,  $[\text{N}] = 2.4 \times 10^{12}$ ; triangles,  $[\text{N}] = 3.6 \times 10^{12}$ .

The yield of atomic oxygen ( $\text{O}^3\text{P}$ ) was measured at room temperature in excess N. Figure 4 shows the O atom signal produced in the titration of NO and NO<sub>2</sub> with initial N concentrations of  $2.4$  and  $3.6 \times 10^{12} \text{ molecules cm}^{-3}$ . These concentrations were not quite large enough to drive (R2) to completion in the 55-ms reaction time. In Figure 4, the data have been corrected for the incomplete conversion using the rate constants determined in this work. This correction is less than 20% for the lowest N-atom concentration. (Attempts to further increase the N-atom concentrations resulted in a large increase in H and O impurity production by the source). The oxygen atom yields are equal for the two reactions.

The product analysis is consistent with (R2a) being the only channel, as suggested by *Clyne and McDermid* [1975]. Reaction (R2d) is unlikely to be important; to proceed adiabatically (i.e., to conserve spin multiplicity), it would require a quintet transition state, which is likely to have a large barrier. This experiment cannot completely rule out (R2b) and (R2c). If the branching ratios of these two channels were equal, the measured



**Figure 5.** Arrhenius plot of the reactions N + NO and N + NO<sub>2</sub>. Lines are the reported rates derived from a weighted least squares fit to all the data. The  $2\sigma$  uncertainties (precision) for the individual data points are listed in Tables 1 and 3.

**Table 4.** Literature Comparison for  $N + NO_2 \rightarrow$  Products

Reference	$k(298)^a$	$k(T)^b$	Method <sup>c</sup>
This work	$1.2 \pm 0.1$	$(5.8 \pm 0.5) \exp[(220 \pm 50)/T]$	DF-RF
Verbeke and Winkler [1960]	—	$8 \pm 1$ at $T = 500$ K	DF-VA
Phillips and Schiff [1965]	$1.8 \pm 0.2$	—	DF-MS
Clyne and McDermid [1975]	$0.14 \pm 0.02$	—	DF-MS
Husain and Slater [1980]	$3.8 \pm 0.1$	—	FP-RF
Clyne and Ono [1982]	$0.30 \pm 0.07$	—	DF-RF
DeMore et al. [1992]	$0.3^{+0.6}_{-0.2}$	—	review

<sup>a</sup>  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup><sup>b</sup>  $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup><sup>c</sup> FP, flash photolysis; RF, resonance fluorescence; DF, discharge flow; MS, mass spectroscopy; VA, volumetric analysis

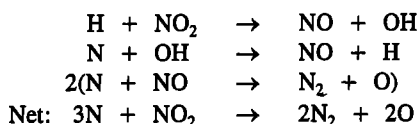
O atom yields in excess N would still be one as each NO produced by (R2b) would react with N to give one O atom.

The temperature dependence of (R2) was determined from 223 K to 369 K and is shown in Figure 5. From a weighted least squares fit of all the data, including an estimate of the systematic errors, we find

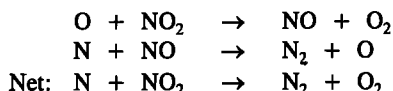
$$k_2'' = (5.8 \pm 0.5) \times 10^{-12} \exp[(220 \pm 50)/T] \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

Table 4 gives the previous measurements of the room temperature rate constant. The reported rate constants vary by over an order of magnitude. Our value is 4 times larger than the value of Clyne and Ono [1982] which has been accepted in recent reviews.

It has been noted that the measurement of this rate constant is subject to catalytic interferences from both hydrogen and oxygen [Clyne and McDermid, 1975; Clyne and Ono, 1982]. Both can be produced as impurities in discharge N-atom sources, and in addition, oxygen atoms are produced in (R2a). Hydrogen impurities react very quickly with  $NO_2$  producing NO and OH, which in turn are very reactive toward N. This scheme is catalytic in hydrogen:



Oxygen atom discharge impurities and product from (R2a) can also react catalytically with  $NO_2$ :



These interferences lead to an enhancement of the observed rate constant. Clyne and Ono [1982] and Clyne and McDermid [1975] noted that the measured second-order rate constant decreased as the stoichiometric ratio,  $([NO_2]/[N])_0$  increased. They attributed the large observed curvature in their  $k'$  versus concentration plot to the interferences noted above. At very high stoichiometric ratios ( $>80$ ), the apparent rate constant reached an asymptote, which Clyne and McDermid measured to be  $1.4 \times 10^{-12}$ , and Clyne and Ono reported to be  $3.0 \times 10^{-12}$ .

The authors argued that this was the true bimolecular rate because at very high stoichiometric ratios the reactivity of N will be dominated by loss to  $NO_2$ .

The method used in this study differs from the work of Clyne and Ono only in that our N-atom detection threshold was lower and the initial N concentrations could be much smaller, thereby reducing the interference from the product of (R2a) to a negligible level. Furthermore, by measuring the H and O impurities in the flow tube we could directly insure that the kinetics would not be subject to the interferences noted above. No curvature was noted in any of the experiments, even at stoichiometric ratios far less than 80.

The lack of impurities and secondary chemistry is also evident in the low reactivity of N atoms with ClOCl and  $Cl_2$  measured with the same apparatus. An upper limit for the reaction of  $N + ClOCl$  at 373 K was determined to be  $3 \times 10^{-16}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> [Stevens and Anderson, 1992]. For  $N + Cl_2$  at 387 K an upper limit of  $5 \times 10^{-16}$  was measured. Both these measurements are very sensitive to radical impurities.

It is not obvious how to explain the results of Clyne and Ono. It is possible that they had an unidentified  $NO_2$ -dependent background signal from excited states of  $N(^2D, ^2P, \text{ or } ^2S)$  or from reactions of  $N_2(A^3\Sigma)$  with  $NO_2$  or the  $N_2O$  product.

The rate reported here is 3 times slower than that measured by Husain and Slater [1980] using flash photolysis. As mentioned earlier, this N-atom source produces copious concentrations of  $O(^1D)$ . Ground state N atoms are only produced after quenching of the excited state N photolysis products. The  $N_2O$  photolysis source seems inappropriate for the study of ground state N-atom kinetics, especially for reactions that are known to be sensitive to radical impurities.

## Conclusion

### Reaction Mechanisms

As demonstrated by the fast reaction rates and slightly negative activation energies, it is clear that both (R1) and (R2) proceed through "loose" early transition states. The dominant orbital interactions at the transition state will be between one of the lone p-orbital electrons on the N with the radical electron of NO ( $\pi^*$ ) or  $NO_2$  ( $a_1$ ). Polanyi and Wong [1969] have shown that for this type of potential energy surface, a large fraction of the exothermicity will be disposed of as vibrational excitation of the products. This is exactly what has been observed for both of these reactions [Clough and Thrush, 1969; Black et al., 1973].

To show the generality of the electronic structure of the transition state, it is instructive to compare the observed reaction kinetics of N atoms with the high-pressure limits for the association reactions of other radicals with NO and  $NO_2$ . Although these reactions will proceed to form stable adducts, we expect the radical-radical interactions at the transition states to be very similar. The high-pressure rate constants for the reactions of OH, O, ClO, BrO, F, FO, Cl, Br, I with NO and  $NO_2$  [DeMore *et al.*, 1992; Howard and Smith, 1983] are all within a factor of 5 of the rates of (R1) and (R2). Most of these reactions also display little or no temperature dependence.

### Atmospheric Implications

Compared with the Jet Propulsion Laboratory recommended values of  $k_1''$  and  $k_2''$ , these new measurements will decrease the modeled lifetime and thus the modeled concentration  $NO_x$  in

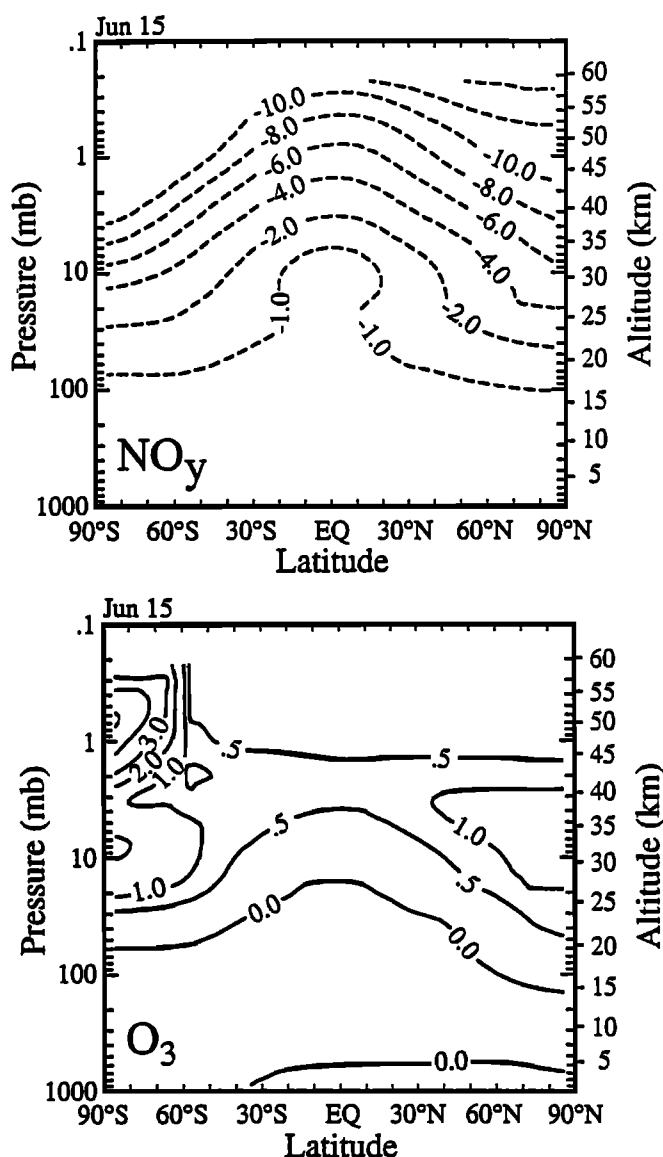
the upper stratosphere and mesosphere. Although the discrepancy is largest for  $k_2''$ , it is of minor importance because of the small mixing ratios of  $NO_2$  at these altitudes. The slight negative temperature dependence of (R1) has a larger impact: at 220 K the rate is 35% faster than the accepted value. A two-dimensional model from Atmospheric and Environmental Research, Incorporated [Ko *et al.*, 1993] was used to investigate the effect of this change to the chemical kinetic database. Figure 6 shows the calculated percent change (compared to the Jet Propulsion Laboratory recommended rate) in ozone and  $NO_y$  for June 15. As expected, the largest changes occur in the high-latitude upper stratosphere and lower mesosphere. The calculated changes are, however, small and result in little change to the calculated ozone column.

The temperature dependence of (R1) has recently been the subject of speculation. In a model of the Martian thermosphere, Fox [1993] speculated that this reaction slowed down at very cold temperatures (130–160 K); these results show that just the opposite occurs, at least down to temperatures of 220 K. To explain anomalously low concentrations of N atoms in the Earth's thermosphere (where temperatures are as high as 1000 K), Siskind and Rusch [1992] also speculated that (R1) had a positive temperature dependence. The measurements described here certainly do not preclude the possibility that the temperature dependence could exhibit non-Arrhenius behavior. Indeed, some recent measurements at high temperatures suggest that the rate may increase slightly with increasing temperature [Michael and Lim, 1992; Davidson and Hanson, 1990].

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**Figure 6.** Shown is the calculated percent reduction in  $NO_y$  and the resulting small percent increase in ozone in a two-dimensional model [Ko *et al.*, 1993] when the rate for (R1) is changed from the Jet Propulsion Laboratory recommendation to the value determined in this study.

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